PREPARATION OF CHEMICALLY MODIFIED AND HYPERCROSSLINKED MICROSPHERES OF POLY(ACRYLONITRILE-*co*-DIVINYLBENZENE-80-*co*-VINYLBENZYLCHLORIDE) AS SORBENTS TO CAPTURE PHARMACEUTICAL RESIDUES.

Nur Nida Syamimi Subri [1], Siti Nurul Ain Md. Jamil [1,*] Mohd Farid Ismail [1]
Tasnim Munshi, [2] Ian J. Scowen [2] & M. Rashidi Abdull Manap[1,2*]
[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
[2]School of Chemistry, University of Lincoln, Joseph Banks Laboratories, Green Lane, Lincoln, Lincolnshire, LN6 7DL, UK

corresponding author: *ctnurulain@upm.edu.my* ***and*** *rashidichemistry@upm.edu.my*

ABSTRACT

Residues of pharmaceutical are potentially hazardous contaminants to aquatic life and human. Pharmaceutical residues have been detected in Malaysian tropical wastewaters. A challenge therein is the development of enrichment techniques able to extract polar pharmaceutical residues, since these compounds are widely found in aqueous samples yet present particular difficulties in their extraction due to their polar character. Acrylonitrile (AN)-divinylbenzene-80 (DVB-80)-vinylbenzylchloride (VBC) porous terpolymer material was prepared in the present research *via* precipitation polymerisation method. The porous terpolymer (MNA1) containing chlorine pendant groups was hypercrosslinked *via* a Friedel Crafts reaction to develop 3D network structure within the terpolymer chains. FT-IR spectrum of MNA1 showed that the chloromethyl groups derived from VBC were consumed, which was consistent with successful hypercrosslinking. The hypercrosslinked porous material was then chemically modified with ethylenediamine (EDA) (MNA2) to develop active functional groups (diamine moisties) along terpolymer chains. FT-IR spectrum showed that a new diamine absorption band appeared after the chemical modification, indicating the nitrile group was successfully converted into diamine moieties. Both experimental spectra was validated and proved by the calculated transmittance spectra. The mono-disperse spherical particles of MNA1 and MNA2 were observed using SEM analysis. Their high specific surface area and polar character (arising from AN residues), make them as potential materials to extract pharmaceutical residues.

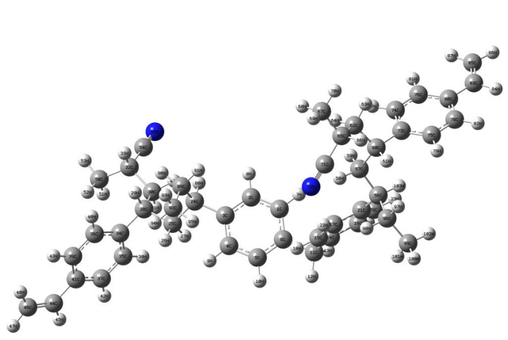
INTRODUCTION

Residues of pharmaceuticals have become the emerging class of pollutants due to their ubiquitous nature, toxicity and persistency in the environment. The reports of widespread pharmaceutical contamination of lakes, streams, and ground waters have been increasingly documented worldwide, including in Malaysian wastewater specifically in river and effluents sewage treatment plants [1]. Pharmaceutical residues are usually polar compounds and biologically active at low concentrations. The traces of pharmaceutical residues were detected in drinking water and in cooked seafood that may potentially risk the safety of consumer either through direct effect or indirectly through potential antimicrobial resistance. There is a risk for acute and chronic effects in the environment inherent to the release of pharmaceutical residues in water as some of the drugs are endocrine disrupting compounds (EDCs), capable of causing sexual under-developments, infertilities and disrupt sexual behaviors that are deleterious for the entire aquatic ecosystem. Continuous releases and chronic exposure to these chemicals can result not only in subtle effects on aquatic species but also could pose a risk to human health associated with consuming contaminate drinking water over a lifetime.

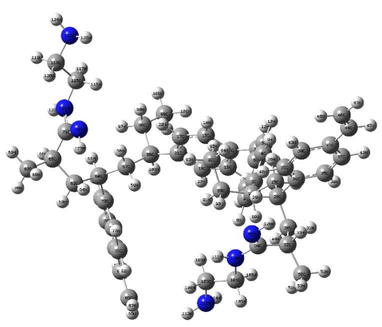
In this research, our approach is to facilitate the extractions of polar pharmaceutical residues is to produce a novel sorbent with higher capacity, and selectivity; that is known as ethylenediamine (EDA) modified-hypercrosslinked (HXL) poly(acrylonitrile (AN)-co-divinylbenzene-80 (DVB-80)-co-vinylbenzylchloride (VBC)) terpolymer sorbent. The presence of polar moiety (from acrylonitrile unit) and active functional group (from amines moiety) in the modified sorbent are expected to enhance ion-exchange interaction between organic compounds and the sorbent. DVB-80 is a useful monomer to install porosity in terpolymer system; while VBC monomer was incorporated to develop 3D network structure to form hypercrosslinked terpolymer sorbent.

The sorbents are more stable than all silica-based mixed mode media and capable to extract a wide range of pharmaceutical residues from water matrices. The chemically EDA-modified HXL poly(AN-co-DVB-80-co-VBC) terpolymer in the form of mono-disperse microspheres are sorbent particles with high specific surface area (SSA) and thus provide high adsorption capacity with better selectivity to capture targeted analytes. The calculated vibrational spectra was obtained to prove the experimental formation of novel EDA-modified HXL poly(AN-co-DVB-80-co-VBC).

Optimized Geometry of Terpolymers



HXL POLY(AN-*co*-DVB-80-*co*-VBC) (MNA1)



EDA-MODIFIED HXL POLY(AN-*co*-DVB-80-*co*-VBC) (MNA2)

METHODOLOGY

SYNTHESIS

HYPERCROSS LINKING

CHEMICAL MODIFICATION

CHARACTERIZATION

STRUCTURAL STUDY

- ATR-FTIR
- QM calculations
- SEM IMAGES
- POROSITY

CONCLUSION

- MNA1 and MNA2 were successfully synthesized and characterized by using FT-IR spectra analysis.
- The experimental and calculated vibrational spectra of the new chemically-modified hypercrosslinked terpolymer were comparable.
- The IR spectra of MNA2 showed the disappearance of CN absorption band and a new diamine functional groups appeared, which was coming from NH stretching absorption peak in the terpolymer system, indicates that the chemical modification was successful.
- Hypercrosslinking of MNA1 via a Friedel-Crafts reaction gave rise to a significant increase in the specific surface areas up to 983 m^2/g.

ACKNOWLEDGMENT

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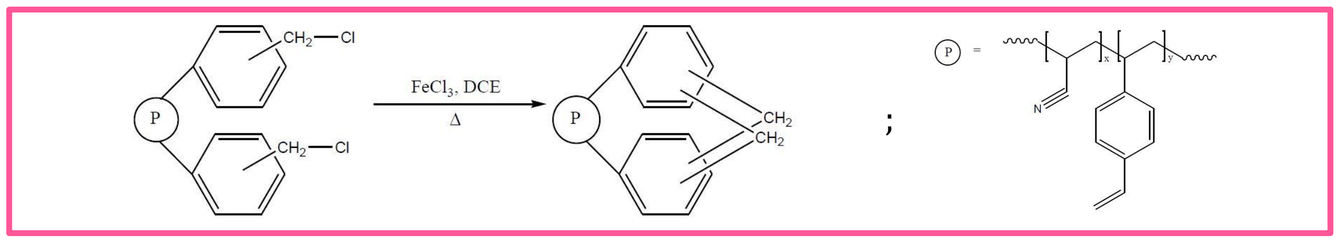
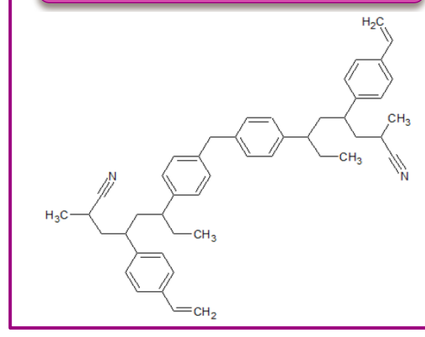
RESULTS AND DISCUSSION

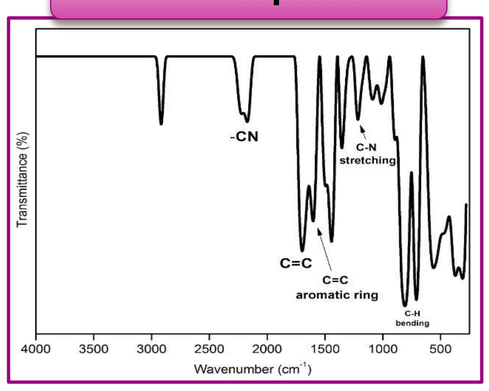
Reaction scheme of MNA1



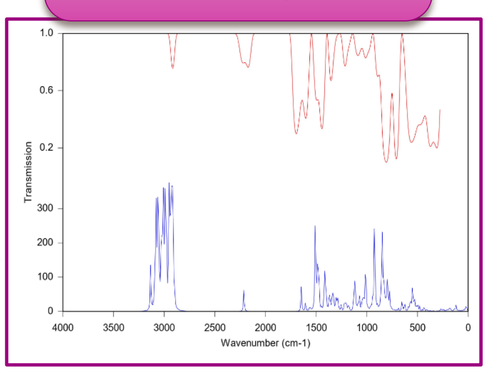
Molecular Structure



ATR-FTIR spectrum

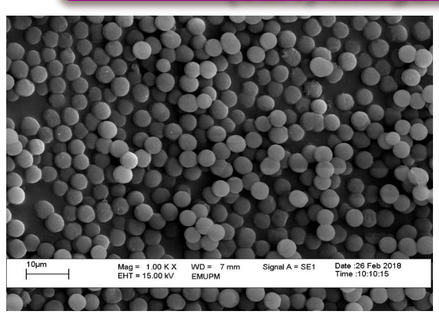


Validation of experimental ATR-FTIR spectrum with the calculated transmittance spectrum



MNA1

Scanning Electron Microscopy (SEM) Image

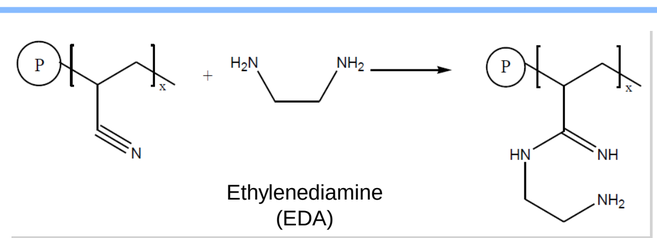


The **hypercrosslinked terpolymer** particles is in the form of spherical **monodisperse** beads with mean particle diameter of **1.9 µm**.

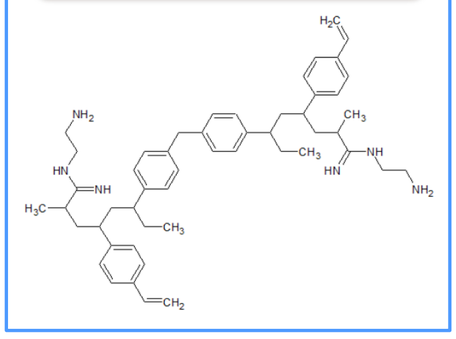
Porosity Analysis Data

HXL Poly(AN-*co*-DVB-80-*co*-VBC)	Surface area (m^2/g)	Volume pores (cm^3/g)	Pore size (nm)
	983	0.731	3.0

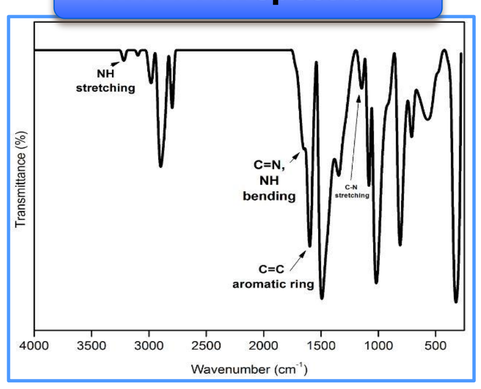
Reaction scheme of MNA2



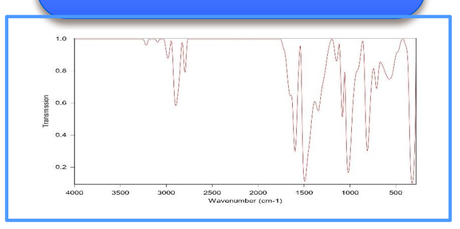
Molecular Structure

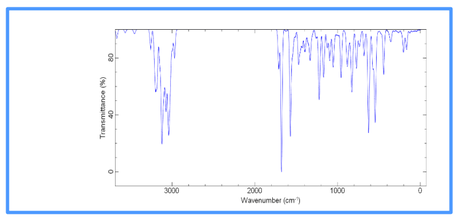


ATR-FTIR spectrum



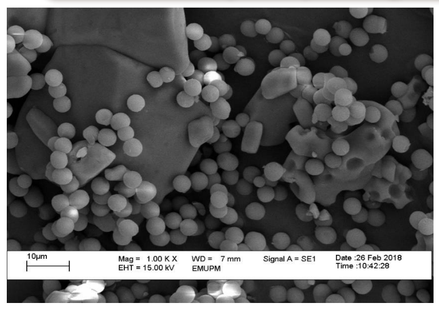
Validation of experimental ATR-FTIR spectrum with the calculated transmittance spectrum





MNA2

Scanning Electron Microscopy (SEM) Image



The **EDA-modified hypercrosslinked terpolymer** particles also obtain spherical **monodisperse** particles with mean particle diameter (**1.5 µm**).

Porosity Analysis Data

EDA-Modified HXL POLY(AN-*CO*-DVB-*CO*-VBC)	Surface area (m^2/g)	Volume pores (cm^3/g)	Pore size (nm)
	0.321	0.105	1303.3